

CEMENT AND LIME MANUFACTURE

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Composition of Portland Cement.

EFFECT OF ADDED MATERIALS ON AQUEOUS EXTRACTS.

AN investigation has been made by Messrs. G. Z. Kalousek, C. H. Jumper and J. J. Tregoning on the composition and physical properties of aqueous extracts from Portland cement clinker pastes to which gypsum, calcium chloride, calcium acetate, fluosilicic, sucrose, TDA, tannic acid, and triethanolamine had been added. The results are published in Research Paper No. 1530 of the United States National Bureau of Standards, of which the following is an abstract.

Mixtures of twelve commercial Portland cement clinkers and water were filtered at seven minutes and at two hours after mixing, and the chemical composition, pH, conductivity, surface tension, and density of the extracts were determined. In the majority of the extracts, soda and potash were present in greater amounts than any of the other dissolved oxides. Relatively high concentrations of sulphate occurred in the extracts of the clinkers that contained the larger amounts of potash. The lime concentration and basicity of the extracts were largely determined by the amounts of alkali oxides present. The concentration of silica corresponded approximately to the reported solubility of silica in lime solutions. Low concentrations of oxides of the R_2O_3 group were found, except in extracts from pastes containing the added organic materials. Because the amounts of extractable soda and potash in cements and their possible effects on the properties of concrete have been much discussed subjects for many years, the clinkers used in this study were chosen to give a large range in soda and potash contents. The soda content varied from 0.02 to 0.87 per cent. and the potash content from 0.05 to 1.32 per cent. The clinkers represented standard, moderate-heat-of-hardening, and sulphate-resisting cements. One clinker (low Fe_2O_3) had a high ignition loss and high free-lime content. The clinkers, in 600-lb. batches, were ground to finenesses ranging from 1,760 to 2,260 square centimetres per gramme. The cements were prepared by adding a finely-ground

commercial gypsum (46.7 per cent. of SO_3 , 20.1 per cent. ignition loss) to the ground clinkers in such amount that the mixtures contained 1.75 per cent. of SO_3 as gypsum. Agreement of the analytical determinations of SO_3 made on random samples indicated that uniform mixtures were obtained when the clinker-gypsum composite had been mixed for two hours in a ball mill containing a few pebbles; such mixing had no detectable effect on fineness.

The following materials in percentages by weight of clinker were dissolved in the mixing water used in preparing the pastes:

Calcium chloride	1.456*
Calcium acetate	1.347*
Fluosilicic acid	0.330*
Sugar	0.050
Tannic acid	0.200
Triethanolamine	0.100

TDA, defined as a mixture of "triethanolamine and highly-purified soluble salts of modified lignin sulphonc acids," was dissolved in water (1 TDA : 7 H_2O by weight) and the solution sprinkled on the ground clinker. The mixture, which contained 0.033 per cent. of TDA and 0.23 per cent. of added water, was immediately placed in a ball mill with a few pebbles and mixed for two hours. It was not used for making up pastes until about 24 hours after mixing.

A batch of 7,000 gr. of clinker or cement, plus 2,450 gr. of water (cement-water ratio = 2.86) or solution containing the additional agent, was mixed by hand for $2\frac{1}{2}$ minutes. Immediately after completion of the mixing the paste was placed in an air-pressure filter and as much of the solution was removed as was permitted by the water retentivity of the paste. The average time of contact of hydrating clinker and solution was about seven minutes. A second corresponding mixture was also prepared. This was aged for 1 hour 55 minutes and then remixed and filtered as the first. In order to remove the air which had dissolved during the pressure filtration, all solutions were refiltered through a hardened filter paper into a partially evacuated flask; this eliminated the formation of bubbles in the conductivity and surface-tension cells and in the picnometer. Precautions against contamination of the filtrates by the CO_2 of the air were taken by the use of soda-lime tubes.

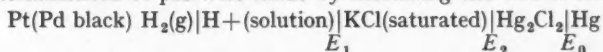
The filtrates were aliquoted into desired amounts for the various analytical procedures shortly after filtration. The basicity was obtained by titrating the filtrates with standardised HCl, using phenolphthalein as the indicator. The average time of contact of the other aliquots of the basic solutions with glass receptacles prior to addition of HCl was about 20 minutes. The solutions were analysed for SiO_2 , R_2O_3 , CaO, MgO, SO_3 , Na_2O , and K_2O . The amounts of Al_2O_3 and Fe_2O_3 were generally determined when the R_2O_3 precipitate was comparatively large. Cr_2O_3 was estimated when its presence was indicated by a green colour of the ignited R_2O_3 . The amounts of Cl, CH_3COO , and F were determined with calcium chloride, calcium acetate, and fluosilicic acid respectively,

* Anhydrous basis.

and were added to the mixing water. Standard procedures of analysis were followed, blank determinations being made and corrections applied. SiO_2 , R_2O_3 , CaO , MgO , Na_2O , K_2O , SO_3 , and Cl were determined gravimetrically. Cr_2O_3 was estimated colorimetrically. Fe_2O_3 was determined volumetrically by titration with $\text{K}_2\text{Cr}_2\text{O}_7$. Na_2O was precipitated and weighed as sodium uranyl zinc acetate. K_2O was precipitated as potassium chlorplatinate, which was reduced to Pt and the Pt weighed. Acetate was determined titrimetrically on distillates from mixtures of the original solutions plus H_3PO_4 . Fluorine was determined according to a method reported by Hoffman and Lundell.

Immediately after filtration, portions of the solutions were transferred to the receptacles used in the determination of pH, conductivity, surface tension, and density. These were placed in an air bath, which maintained the temperature of the solutions at $25 \text{ deg.} \pm 0.39 \text{ deg. C.}$

The determinations of pH were made by measuring the emf of the cell, E_c ,



at 25 deg. C. with a calibrated potentiometer, using a sensitive galvanometer and a standard cell. The pH values of the solutions, after the values of E_c had been measured, were computed from the relation

$$\text{pH} = \frac{E_c - (E_1 + E_2 + E_0)}{0.05914}$$

in which E_0 is the standard potential of the saturated calomel electrode, and E_1 and E_2 represent the potentials developed at the liquid junctions.

Alkalis (K_2O and Na_2O).—The maximum concentrations of alkalis in the extracts from the untreated clinker pastes were 2.99 grammes per litre of Na_2O and 18.65 grammes per litre of K_2O at seven minutes and 3.89 grammes per litre of Na_2O and 19.71 grammes per litre of K_2O at two hours. The relatively large amounts of K_2O in the extracts from some clinkers are attributed to the presence of K_2SO_4 . In general, smaller amounts of alkalis were extracted in the interval between seven minutes and two hours than during the first seven minutes. The results indicate that large differences may exist among clinkers with respect to the rate of solution of the alkalis. In all the clinkers considerable amounts of alkalis remained undissolved at two hours. Pastes containing gypsum and triethanolamine represent the extreme effects of the addition agents on the extractions of alkalis—gypsum causing the greatest decreases and triethanolamine the greatest increases. The percentages of soda and potash in solution at seven minutes varied from 0.4 to 30 and 1 to 58 respectively. The rate of solution of K_2O from clinkers between seven minutes and two hours varied between 0 and 9 per cent., and of Na_2O between 1 and 12 per cent. The values with added gypsum were from 1 to 8 per cent. for K_2O and 1 to 7 per cent. for Na_2O . In the presence of triethanolamine the rate of solution of the K_2O (from six clinkers) varied between 2 and 10 per cent., and of Na_2O from 2 to 21 per cent.

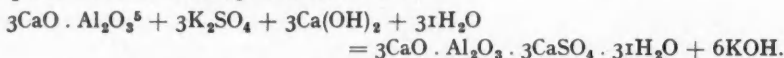
Lime.—The amounts of CaO in solution exceeded the normal saturation values in ten of the twelve 7-minute extracts and in all of the 2-hour extracts.

The data do not fall on a smooth curve because the degree of supersaturation undoubtedly varied among the filtrates. Also in the case of the high-potash clinkers the presence of SO_3 may have affected the solubility relations. A qualitative verification of the supersaturation of the solutions was obtained by visually estimating the amounts of crystalline material precipitated after two months from the various filtrates sealed in glass tubes. The crystals, identified as $\text{Ca}(\text{OH})_2$, were as much as 1 mm. in cross section.

Silica.—An increased concentration of silica in the extracts was accompanied by a decreased concentration of lime. Apparently the effect of the alkalis on the lime concentration does not greatly alter the silica-lime relation. Flint and Wells and Bessey have demonstrated that the compositions of the hydrous calcium silicates are dependent on the composition of the solution. Thus, as the concentration of lime in solution is decreased, the precipitated calcium silicate hydrate becomes poorer in lime. The observed correlation of the CaO-SiO_2 data in the present investigation suggests that lime-poor silicates may be precipitated in the clinker pastes as the lime concentration in the solution is decreased.

R_2O_3 Group (Al_2O_3 , Fe_2O_3 , and Cr_2O_3).—The concentration of R_2O_3 varied from 0.001 to 0.033 gramme per litre at seven minutes and from 0.001 to 0.018 gramme per litre at two hours. The 7-minute filtrates showing the highest R_2O_3 contents contained Cr_2O_3 ; at two hours, however, the constituent was present only in the extract from one clinker. All solutions containing Cr_2O_3 were yellow, indicating the presence of the chromate ion. The portions of R_2O_3 as Al_2O_3 plus Fe_2O_3 varied from 0.001 to 0.017 gramme per litre in the filtrates from pastes containing no added materials. When the organic addition agents were incorporated in the pastes, relatively large concentrations of Fe_2O_3 and Al_2O_3 were sometimes obtained.

SO_3 .— SO_3 was present in significant amounts in filtrates from three pastes at seven minutes, but decreased in the interval between seven minutes and two hours. These decreases appear to be caused by the precipitation of calcium sulphoaluminate according to the reaction:



The evidence for the occurrence of this reaction is based on calculations which show that the equivalents of SO_4 precipitated in the interval between seven minutes and two hours are equal to the increase in equivalents of OH^- during the same interval, allowance being made for the OH^- that was introduced by further changes in the concentration of the alkalis and lime. For the filtrates containing the larger amounts of SO_3 at seven minutes from clinker pastes alone, and with TDA, tannic acid, and fluosilicic acid as added materials, the total increase in OH^- concentration exceeds the total decrease in SO_4 concentration. This is accounted for by the changes in the concentrations of NaOH , KOH , and $\text{Ca}(\text{OH})_2$ in the extracts between seven minutes and two hours. If the OH^- introduced from these sources is deducted from the total increase in OH^- concentration, the increases in OH^- caused by the sulphoaluminate reaction are

obtained. These values are in close agreement with the decreases in SO_4^{--} concentration. In many instances the sulphoaluminate reaction accounts for the small amounts of SO_3 in the filtrates at seven minutes.

pH and Other Constants.—Constant emf was not attained in many of the pH determinations. This may have been due to the presence of so-called "electrode poisons" (traces of sulphur compounds, ferric and chromate ions, etc.). Although as long as six hours was frequently allowed for approaching a constant emf, the values obtained in many determinations appeared to be low. Because of the uncertainty of such results, and since the filtrates consisted essentially of mixtures of calcium and alkali hydroxides and their salts, the pH values of pure solutions of calcium hydroxide and potassium hydroxide were determined. The use of triethanolamine resulted in such large potential disturbances that emf measurements could not be made. The rather consistently low values obtained on filtrates when TDA was present are also attributed to electrode poisons. Practically all the other low results on the filtrates, except those containing the calcium salts as added materials, may result from the same cause.

The effect of highly-soluble calcium salts lowered the pH of the extracts by relatively large amounts, due to the decreased effective concentration of the hydroxyl ion in the solutions. Gypsum, because of its lower solubility, decreased the pH by only 0.02 to 0.04 unit at the basicities prevailing in the extracts. The excellent agreement between the pH values for $\text{Ca}(\text{OH})_2$ solutions, from 0.04 to 0.015 equiv/litre, reported by Lea and Bessey and those reported here is of interest because different methods of calculating pH were employed. The introduction of relatively large amounts of sulphates, chlorides, or acetates in some of the extracts, resulting from the addition of calcium salts, accounts for the increased conductivity of such solutions. The surface-tension data range from 72 to 73 dynes per centimetre. The higher values were obtained on solutions containing calcium chloride and acetate as additions. It has occasionally been suggested that changes in surface tension of the aqueous phase of cement pastes may affect such properties as workability. It seems doubtful, however, that the relatively small observed changes in values could be given much weight in interpreting such properties of the pastes.

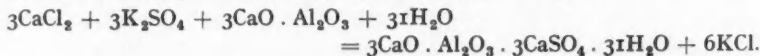
Gypsum.—Gypsum was the only added material which consistently decreased the extraction of the alkalis from the clinkers, although in a few cases the decreases were insignificant.

Calcium Chloride.—Calcium chloride produced larger changes than did gypsum. This may be due to the greater solubility of calcium chloride, which permitted more complete neutralisation of the alkali hydroxides according to the equation



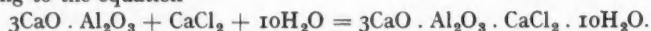
Calcium chloride also differed from gypsum in that, on the average, it increased the extractions of the alkalis from the clinkers. At two hours, particularly, the trend of increased potash concentration is very uniform. In the presence of calcium chloride, the sulphoaluminate reaction appears to be greatly accelerated,

as indicated by the large decreases in SO_3 concentration, leaving only small amounts in solution. The sulphoaluminate may precipitate from pastes of clinkers containing potassium sulphate according to the reaction



This reaction would account for the smaller amounts of lime present in the extracts from the clinkers containing potassium sulphate.

The quantities of lime remaining in solution are governed by the extent of precipitation of calcium chloroaluminate as well as by the neutralisation and sulphoaluminate reactions. The formation of the chloroaluminate proceeds according to the equation



General trends of lowered concentrations of both silica and R_2O_3 occurred in the extracts containing calcium chloride. In most cases the decreases were greater at seven minutes than at two hours.

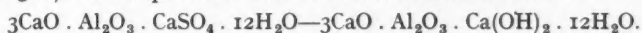
The decreases in the concentration of the chlorine from that added as calcium chloride (26.62 gr. of Cl per litre) are attributed largely to the formation of the chloroaluminate. Previous work has shown that the composition of this compound does not vary much from the formula $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ in the presence of concentrations of calcium chloride such as prevail in the extracts. The results indicate that only small amounts of Al_2O_3 reacted with the calcium chloride during the two periods.

Calcium Acetate.—The changes caused by the presence of calcium acetate in the extracts are very similar both in magnitude and direction to those induced by calcium chloride. The basicities of many of the extracts are governed largely by the neutralisation reaction between the alkali hydroxides and the added salt. The amounts of lime in the extracts are somewhat smaller than those in the extracts containing calcium chloride (note that smaller amounts of calcium acetate were added to the pastes). The remaining alterations show no marked departures from those produced by calcium chloride, except that some extracts of the low-potash clinkers contained appreciably more R_2O_3 in the presence of calcium acetate. A white turbid appearance of ten of the twelve 7-minute extracts and of one of the 2-hour extracts indicated that some of the constituents of these solutions were present in the colloidal state. The acetate added to the pastes was withdrawn from the extracts, probably in part by precipitation as an acetoaluminate and in part by absorption, as indicated by the decreased concentration of acetate in solution at seven minutes. Although further decreases in acetate concentration occurred between seven minutes and two hours in extracts of five of the clinkers, increases were found in the seven remaining extracts.

Fluosilicic Acid.—The changes produced by fluosilicic acid were generally small. Fluorine was found in the extracts in amounts varying between 0.00 to 0.11 and 0.00 to 0.18 gramme per litre at seven minutes and two hours, respectively. The small amounts of fluorine in the extracts at seven minutes show that the

constituents of this material were rapidly precipitated. The minor alterations in basicity and SO_3 were decreases for the most part. Changes in the extractions of soda were small, but the extractions of potash are of interest in that they were decreased at seven minutes and altered only slightly at two hours. Precipitation of calcium fluoride from the extracts may be indicated by the generally decreased concentration of lime in the extracts at both seven minutes and two hours.

Sucrose.—Sucrose is the only one of the added materials considered thus far that increased the basicity of the extracts. This was caused not only by increased extraction of the alkalis but also, to a greater extent, by the almost complete conversion of dissolved potassium sulphate to potassium hydroxide, according to the sulphoaluminate reaction. Only 0.03 to 0.15 gramme per litre of SO_3 remained in the 7-minute extracts of the clinkers which contained the larger amounts of SO_3 . At the same time, the lime concentrations of 0.04 to 0.07 gramme per litre were lower than those corresponding to saturation values for the respective potassium hydroxide concentrations. The large quantities of lime required for the precipitation of the sulphoaluminates may account for the apparent under-saturation. The large increases in the amounts of R_2O_3 , consisting wholly of alumina, in the 7-minute extracts of these clinkers may therefore be due to the low-lime concentration in the filtrates. This is supported by the observation that, as the CaO concentration increased in the interval between seven minutes and two hours, the alumina concentration decreased to values approximating those of untreated filtrates. The alumina was precipitated presumably as a calcium aluminate hydrate, although the reactions of the aluminous compounds in the clinker after the sulphate had combined as a sulphoaluminate are not yet definitely known. On the basis of recent results both the monosulphate and trisulphate sulphoaluminates are metastable in the presence of alkali hydroxide (0.1 to 0.5 *N*) with respect to members of the solid-solution series



Therefore, as the aluminous compounds continue to react, the basicity having increased due to the sulphoaluminate reaction involving potash, a conversion of the metastable products to members of the solid-solution series might be expected. However, this conversion occurs but slowly, and calcium aluminate hydrate is probably precipitated as such during the period between seven minutes and two hours.

TDA.—Of the various added materials, TDA (plus 0.23 per cent. of H_2O) resembles gypsum the most closely in its effects on the extracts. The decreases in the basicity of the extracts are caused partly by the reduced extractions of the alkalis but perhaps to an even greater extent by inhibition of the sulphoaluminate reaction. Although the reason for the retardation of this reaction is not apparent, the addition of 0.23 per cent. of water during the incorporation of the TDA may have partly prehydrated the clinker. Such prehydration would have been possible, since the TDA (plus 0.23 per cent. of H_2O) was mixed with each clinker on the day preceding the tests. The amounts of R_2O_3 , which consisted partly of Fe_2O_3 and in some cases Cr_2O_3 , were increased in most filtrates at both periods.

Tannic Acid.—Changes caused by the addition of tannic acid were generally small. At seven minutes irregular changes in basicity and potash concentration occur, but at two hours fairly regular increases are apparent. The variations in extractions of soda are small at both time periods. Relatively large decreases in concentration of lime occurred in the 7-minute extracts of a number of low-potash clinkers. Very similar changes were noted in the 7-minute extracts of pastes to which fluosilicic acid had been added. The 2-hour filtrates from pastes with tannic acid show small decreases in lime concentration. At both seven minutes and two hours, tannic acid produced no change in the concentration of SO_3 in the majority of the extracts. In the remainder, small increases or decreases occur. The alterations in the concentration of silica are somewhat irregular at both seven minutes and two hours, but increases predominate. Relatively large increases in the R_2O_3 content of the extracts were found, particularly at seven minutes. These increases may result from the formation of complexes between tannic acid and the R_2O_3 .

Triethanolamine.—Triethanolamine produced greater alterations in the compositions of the extracts than any other added material. Because of rapid setting, extracts of six of the pastes at seven minutes and of two pastes at two hours could not be obtained. The increases in basicity displayed by a majority of the extracts appear to be caused by greatly increased extractions of the alkalis. Where the concentrations of alkali hydroxides were increased, the lime content of the extracts was reduced but still exceeded normal saturation values. No significant alteration of the SO_3 concentration occurred except for a decrease in the extract of the clinker highest in potash. Three extracts showed increases in silica concentration of 0.02 to 0.03 gramme per litre, but the remainder were unchanged. Probably the most striking change in composition of the extracts is the increase in their content of R_2O_3 . As in the case of tannic acid, the increases in concentration of R_2O_3 may result from the formation of complexes between triethanolamine and ferric and aluminum hydroxides.

Summary.

(1) From 1 to 58 per cent. of the total potash and from 0.4 to 30 per cent. of the total soda in twelve Portland cement clinkers were extracted in seven minutes from pastes of these clinkers containing no added materials. In the interval between seven minutes and two hours the percentage increases in the amounts of potash ranged from 0 to 9 and from 1 to 12 for soda. Triethanolamine increased the extraction of the alkalis from the clinkers much more than any other material, and gypsum caused the greatest decreases.

(2) The extracts of the clinker pastes generally contained lime in amounts greater than the normal saturation values for calcium hydroxide. The exceptions, in a few of the sucrose-containing extracts, were apparently caused by rapid precipitation of calcium sulphoaluminate.

(3) The amounts of silica and lime in the extracts corresponded approximately to their reported solubility relations in the system lime-silica-water at 30 deg. C.

(4) The amounts of alumina in solution were small except when organic materials had been added to the pastes. Ferric oxide was either absent or present only in small amounts, except in filtrates containing triethanolamine. Small quantities of chromic oxide were found in some of the filtrates.

(5) SO_3 usually decreased in concentration between seven minutes and two hours, precipitating as a sulphoaluminate. In some instances the changes in concentrations of lime and alumina and the increases in basicity were attributed to the formation of calcium sulphoaluminate.

(6) Notwithstanding the presence of gypsum, a large spread in basicity was shown by the filtrates from pastes containing added gypsum.

(7) Computations based on the amounts of calcium chloride that had combined with alumina in the clinkers up to seven minutes and two hours suggest that only small amounts of the alumina-bearing materials had reacted.

(8) Sucrose accelerated the early reactions involving the alumina-bearing constituents of the clinkers.

(9) The pH-basicity values of filtrates obtained from clinker-water mixtures, with and without added materials, except calcium salts, approached closely to those of the potassium hydroxide curve when electrode poisons were absent. The emf cell, used for measuring the pH of the solutions and filtrates, was calibrated against potassium hydroxide solutions of known pH and concentration. The presence of calcium chloride and calcium acetate in the filtrates caused large decreases in the effective concentration of hydroxyl ion. The addition of gypsum, on the other hand, caused only slight decreases, which amounted to 0.02 to 0.04 pH unit.

X-Ray Analysis in Industry.

DEVELOPMENTS in the methods of examining the behaviour of solids by X-ray diffraction methods were described at a conference on X-ray analysis in industry, held by the Institute of Physics at Cambridge on April 9 and 10. The first session was devoted to a discussion on "The Quantitative Treatment of Powder Photographs," the introductory papers being "The Cylindrical Specimen" by Dr. A. J. Bradley, "The Flat Specimen" by Dr. G. W. Brindley, and "Microphotometers" by Professor J. M. Robertson. The second session opened with a discussion on a proposal to change the present values used for X-ray wavelengths to absolute values, followed by a discussion on "Some Recent Developments in X-ray Diffraction." Dr. A. H. Jay spoke on "Superlattice Formation," Dr. K. Lonsdale on "Thermal Effects and Allied Phenomena," and Dr. H. Lipson on "Side-band Formation." Dr. A. J. C. Wilson closed the session with an interim report on the progress made in the preparation of the index to X-ray diffraction photographs of powders. The last session was devoted to a discussion on "Line Broadening"; Dr. F. W. Jones opened it with a paper on "Quantitative Treatment of Crystal-size Measurement," and was followed by Dr. A. J. C. Wilson on "The Effects of Distortion and other Imperfections."

Cement Carried in Bulk in Ships.

IN order to expedite the loading of ships and to save containers, a pneumatic plant has been installed at a United States port. The cement is taken from the factory to the wharf in bulk containers, from which it is tipped into a pit below ground level. On a track below the pit is a Fuller-Kinyon pump, which pumps the cement from the pit into any one of the six silos built on the ground. The silos have a capacity of 10,000 tons (1,666 tons each), and are constructed with bottoms with a slope of 58 degrees. A bag filter is fitted to the top of the silos, and there is a double rotary valve at each hopper. In another tunnel

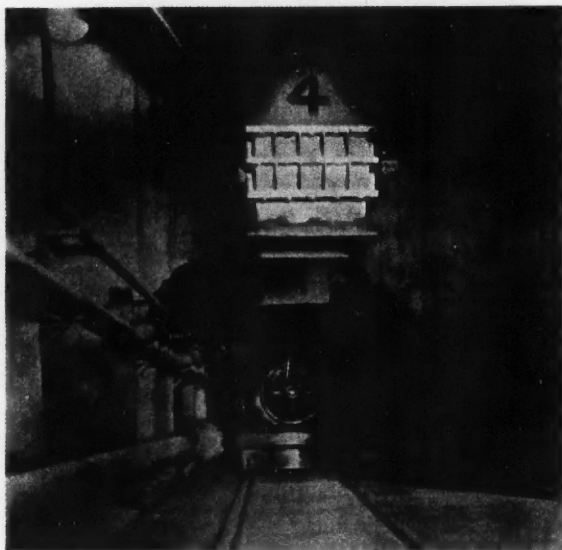


Fig. 1.—Cement Pump in Gallery below Silos.

beneath the silos is another Fuller-Kinyon pump, which pumps cement from the silos to the ship's holds. In one period of 26 hours, 7,330 tons of cement were transported from the silos to a ship. This pump is also on a track, and can be moved into position under the hopper of any one of the six silos (Fig. 1). The pumps have a rated capacity of 166 tons per hour, but have transported up to 180 tons per hour, and, by transferring the first-mentioned pump on to the same track as the second, both pumps can be used to load ships at the same time. The pumps are equipped with 250 h.p., 2,300-volt motors, and air is supplied by two compressors operated by similar motors.

The Storage of Coal.

A PAPER entitled "The Storage of Coal for Industrial Purposes," by Mr. R. A. A. Taylor, M.Sc., has been issued by the Coal Division of the Ministry of Fuel and Power. The author states that most industrial coals may be stored safely if a few simple principles are observed. It may deteriorate in quality while it is in store, but deterioration is not as a rule important. A coal that has been soaked by rain may contain about 10 per cent. more moisture than when it is apparently dry; a ton of the coal picked up may therefore contain only some 18 cwt. of the original coal, although the quality of it may not have depreciated. It is possible to draw a line dividing conditions favourable to safe storage from conditions unfavourable. This line must be used with some flexibility, but it provides useful guidance and is indicated in Table I.

TABLE I.

	Favourable to safe storage.	Unfavourable to safe storage.
<i>Size of coal</i> ..	Nuts, cobbles, round coal; to the exclusion of fine coal in the same heap.	Fines, slack, run-of-mine, alone or included with larger coal; small coal formed by breakage.
<i>Size of store</i> ..	Less than about 200 tons..	Greater than about 200 tons.
<i>Height of stack</i> ..	Not greater than 8 ft. to 10 ft.	Greater than 8 ft. to 10 ft.
<i>Ventilation</i> ..	Adequately promoted; or, what seems easier, effectively suppressed.	Moderate, or natural; if due to passages caused by segregation during stacking, either by a pocket of larger coal or around pillars or against walls.
<i>Age of coal</i> ..	Greater than 3 to 6 months	Up to 10 weeks.
<i>State of coal</i> ..	Having heated and cooled	Freshly wrought.
<i>Type of coal</i> ..	Hard or dull; anthracite, anthracite coal; splint, cannel.	Soft and bright; bituminous, sub-bituminous, lignitic.
<i>Site of stack</i> ..	Most open situations on clean, firm ground.	Near a source of warmth such as a boiler-house wall; or overlying steam pipes or a covered channel through which a warm fluid is passed; or overlying or mixed with oily material or other organic waste.

The evidence imputing an unfavourable character to many other conditions that have been associated with spontaneous heating is inconclusive. Such conditions are, for example, a high content of sulphur or pyrites in the stored coal; the storing of wet coal; storing on a wet site; hot weather following rain; the storing of mixed coals; the storing of unwashed coal; the laying down of fresh coal on old. Most often these conditions could be ignored. Where difficulties have been thought to be due to one or another of them, it is possible that some different cause would be found responsible if all the factors operating could be disentangled. Thus it is possible that it is a mixture of sizes, not of kinds of coal, that contributes to spontaneous heating in mixed coals. A combination of adverse factors may lead to a fire, when one unfavourable circumstance might be without effect.

Size of Coal and Method of Stacking.

The size of the coal is most often the predominant factor in determining whether it will heat spontaneously. Coal that will pass a $\frac{1}{8}$ -in. sieve in all its different forms and associations is the cause of nearly all storage difficulties; coals of mixed sizes, including fines, run-of-mine and "through" coals, are more liable to heat than uniformly fine coal, because the larger pieces of coal open the texture of the heap and facilitate the type of ventilation necessary for heating to proceed. Single nuts are very safe, and larger sizes are quite safe, provided that fines have not been produced during handling. The danger of heating is greater under a chute where the finest coal falls and segregates, or is formed by breakage. When coal is being stacked it should be spread out so that there are no local segregations of sizes and lump coal should be distributed as uniformly as possible among the fine. When a material of mixed sizes is made into a conical heap growing by addition at the apex, the larger lumps tend to roll farthest down the sides of the cone, so that the heap shows a gradation of sizes in a vertical direction, with the largest sizes at the bottom. This means that air can find a comparatively free passage under the heap, which can thus be ventilated in a most undesirable way. The whole of the stacking area should as far as possible be used all the time, the height of the stack being approximately uniform all over the area while the heap is built up. Some advantage is gained if a coal that is to be used in a small size can be stored in a large size and reduced as it is taken from the store for use; it would be less dangerous and suffer less deterioration.

Ventilation.

Ample ventilation makes the stack safe, but is difficult to achieve except in the smallest heaps. Attempts to achieve it in large heaps usually do not go far enough and aggravate conditions already not good. On the other hand, it is difficult to exclude ventilating currents of air, but it is possibly easier to achieve effective results in this way than by promoting ventilation. If ventilation is aimed at, pipes projecting vertically and horizontally into the stack are used. Besides perforated metal pipes, land drainage pipes of unglazed earthenware 7 in. in diameter by 1 ft. long are suitable. The pipes may be arranged at horizontal intervals of 6 ft. to 15 ft. and at vertical intervals of 4 ft. to 6 ft.; perforations or junctions between contiguous lengths (which should not quite touch), should be protected from blockage by a flat piece of coal laid over them. In a long narrow heap the horizontal pipes might best go across the heap opening into the atmosphere on each side. They may open into a horizontal flue running the length of the stack. In a square or round heap, the horizontal pipes may radiate from the centre, where there should be a vertical flue into which they open. Ventilation is usually practicable only in the smaller heaps, and then only when the coal is moved by hand. A system forming a close enough network to give adequate ventilation will often be economically impracticable.

Unventilated air-pockets must be avoided. Uncontrolled currents of air can be reduced by packing the coal uniformly, avoiding segregations of particular sizes, packing the coal tightly, and blanketing the heap with fine coal. Normally there

is little difficulty in this because the fines required for such a procedure are necessarily present in coals that need such treatment. It has even been found advantageous to use a portable crusher at the storage site and prepare fine coal specially for blanketing the heap (M. K. Drewry: The prevention of spontaneous heating in large coal piles. *Combustion*, Feb., 1937, p. 28). Promising results have been obtained by sealing a heap with a skin of asphaltic material (M. K. Drewry, *loc. cit.*). A procedure like this would be most practicable with heaps intended to stand for a long time, and arrangements to apply a road dressing of tar or bitumen might be found satisfactory." Running a steam-roller over a stack has been resorted to, and a small tractor with caterpillar tracks will also compact the coal so as to reduce the movement of air in it; in a very small heap a garden roller will be effective. The heap should be rolled from time to time while it is being built up, not merely after it is finished.

The movement of air is impeded in fine coal if it is wet, as moisture tends to close the voids. For this reason, continuously treating a heap with a fine spray of water is often effective in preventing dangerous conditions from arising, although it will not quench a fire that has already started.

Walling may be effective if it can be done. It consists in building a rough wall of the larger rectangular lumps of coal. A permanent coal-storage site sometimes has a low wall around it to protect the base of the stack, whence ventilating currents start, and if the coal is dumped from high railway lines or down a bank it may be partly enclosed laterally by walls. While this helps to impede ventilation, care must be taken that the coal resting against such a wall, or against piles and pillars supporting overhead roofs or lines, has not packed imperfectly or segregated so as to leave channels through which the adjacent part of the stack may be ventilated by chimney action. The wind naturally affects ventilation, and if ventilation is to be suppressed, an elongated stack should, if possible, be laid down end-on to the prevailing wind.

Size of Stack.

Spontaneous heating cannot occur in very small heaps of coal, and fires have rarely been recorded in heaps of less than 200 tons. Primarily it is the height of the stack that matters. A safe height seems to be about 8 ft., although fires have been recorded in heaps as low as 5 ft., but if the coal is of a suitable size and type it may be safe up to 16 ft.; for hard nut coal the height may go up to 20 ft., and for anthracite and double nuts up to 30 ft. A higher limit may be put on what is regarded as safe if a crane and grab is available. A common practice is to build up a stack in stages, increasing 6 ft. to 10 ft. after six months, or 8 ft. to 16 ft. after nine months, or increasing 6 ft. by 1½ ft. every three months.

Site of Stack.

The site of a stack should preferably be a stone floor or a well-rolled floor of ashes that have been completely quenched or cooled. Open ground is best if it is hard clay or chalk; peaty ground should be dressed with a few inches of ballast or ashes. There is no clear evidence that a wet site is harmful. Storage under cover probably offers no advantage.

Freshly wrought coal heats and fires, if at all, within four to sixteen weeks. In a large deep pile heating may develop more slowly, and persist longer, although it will not necessarily occur to a more dangerous degree. A coal more than eight months old can be regarded as safe if there is no heating in the heap, or if there is heating and it is not increasing. There is no clear evidence to show that weather affects the tendency of coal to heat, except insofar as wind may affect ventilation. Fires often start on the windward side of a stack. Coal may disintegrate under the action of the weather, but this is not likely to affect the heating tendency much. A high content of sulphur—or of pyrites—has been thought to promote spontaneous heating. It is now considered very doubtful whether this is so.

Stack Temperatures.

To see whether coal is heating, metal rods may be inserted 10 ft. to 20 ft. apart in the stack with their ends projecting, and to feel whether the rods are conducting heat out of the stack. A better procedure is to use wrought-iron or steel pipes closed at the lower end and to take temperatures by lowering a thermometer down them. The pipes should be from 15 ft. to 50 yd. apart. The temperatures can be read at various depths at intervals.

It has usually become clear within three to four months whether heating is going to develop dangerously. Once a peak has been passed it is unlikely that heating will become threatening again. Maximum temperatures are often to be found 3 ft. to 6 ft. from the top or side of a stack, more especially near the bottom at the side, or at any point farther in where large coal has formed passages through which air can move freely. Heated zones may in suitable weather be located by the appearance of steam long before they become dangerous.

The limit to which the temperature in a coal stack may be allowed to rise before a state of danger is recognised varies according to circumstances, say, from 95 deg. F. to 160 deg. F. The lower part of this range applies when conditions, chiefly the type of coal, are such as to favour spontaneous heating; the higher part would apply, for instance, to semi-bituminous steam coal and when conditions otherwise are not so favourable to heating. The safe upper limit is most often between 115 deg. F. and 140 deg. F. A slow and steady rise may at the critical temperature take a sudden upward turn indicating a sudden and greatly accelerated rate of rise, and the coal will then inevitably fire unless precautions are taken.

Dealing with a Fire in a Coal Stack.

Water should be applied from a hose all over and around the area affected as soon as the temperature reaches 95 deg. F. to 115 deg. F. If the limiting temperature is reached it is wrong to delay in the hope that conditions will improve. The fire or heated zone is local at first, but may propagate in any direction. At its worst it will only appear sporadically at the surface as flames or a glowing patch. It may be recognised by the appearance of a light grey smoke and a distinctive odour, though usually at this stage the fire is established. The seat of the fire must be dug out by holing, trenching, and cutting valleys; the region must be completely exposed, and the hot coal scattered and cooled. Generally,

spraying with water seems to be useless unless an inordinately large volume of water can be used. Heavy spraying is widely practised, but primarily as a means of retarding heating and restraining the temperature below a critical limit until the stack has passed its peak heating period. To achieve this, spraying seems to be effective provided it is copious enough. Storage under water and in bunkers flooded by tidal water has been effectively practised. Another procedure that can be applied to large storage bunkers consists in keeping the coal in very slow circulation by withdrawing it from the bottom and returning it to the top by means of a conveyor, or in passing a very slow current of cold flue gas into the base of the bunker.

Deterioration.

Coal undergoes some deterioration on being left in store, more or less in proportion to the heating that occurs, and will most often be insignificant. Coal does not deteriorate uniformly in all its properties. Bright and soft coals deteriorate more than hard and dull coals; small coals deteriorate more than large coals, which, if they do not disintegrate, may not change noticeably. The rate and extent of deterioration diminish in the order—lignitic coal, sub-bituminous coal, bituminous coal, semi-bituminous coal, anthracite coal, anthracite; splint and cannel coal may be classed with anthracite.

Bright coal may become dull, and the inclusions of certain inorganic constituents (pyrites, ankerite) become "rusty." This does not in itself affect the quality, except that it may favour disintegration.

A large coal, especially if it is soft, friable, fissured or cut up by mineral partings or pyritic nodules, may disintegrate under the action of the atmosphere and the weather. Disintegration differs from most other forms of deterioration in being due chiefly, if not entirely, to exposure, and is little, if at all, related to heating. Dull coals, and cannel and anthracites especially, weather only very slowly if at all. With small coal, slacks, and duff, disintegration does not matter; but disintegration may be important if the original size of a nut or larger coal is an essential quality; with sized steam coals it may mean an increased loss of combustible material through the grate, and this may produce an illusion of diminished calorific value. With gas nuts of deficient coking power, it may cause incompletely carbonised coal to fall through the extractor of a vertical retort. Disintegration occurs more in the winter than in the summer, and is rarely serious in a single season unless the coal is a susceptible one. There is a limit to the extent of disintegration; a coal never falls away to dust. A weathered coal, which may or may not have disintegrated greatly, may break easily when it is handled again. Similar considerations apply as to disintegration. An increase in friability is merely a stage in disintegration.

A stored coal loses heating power but the loss is usually small. It averages between $\frac{1}{2}$ per cent. and 1 per cent. per annum; this is often much less than variations in the efficiency with which the coal is used.

A loss in steam-raising power is generally attributed to a loss of calorific value, but if the coal has not heated this is probably the least important cause of the loss

and may be quite insignificant. A considerable change in the moisture content may produce the illusion of a diminished calorific value; loss may also be caused by changes giving rise to difficulty in maintaining the fire-bed efficiency; disintegration, producing smalls that fall unburnt through the grate, a condition applying to sized coals; and loss of coking power is relied on to maintain the coherence of the fire-bed. Generally the loss in steam-raising power is not serious.

The changes in appearance, size and friability occur independently of heating in the stack, and they may conceivably occur extensively while other changes do not go far. The rate at which a coal deteriorates depends on its size in a very important degree; it is largely determined by the ratio between the total area of the surfaces of all the pieces of coal and the total weight of the coal. This ratio is the specific surface. A large coal deteriorates more slowly than a small one of the same kind; often much more slowly, for specific surface increases greatly as size decreases. With the largest sizes of hard coals deterioration may be altogether insignificant; this provides an additional reason for storing a large coal in preference to a small one. But if with a large coal disintegration is extensive, deterioration will generally be more noticeable. Deterioration occurs most rapidly at first, during the first three to twelve months of storage for example, and then its rate falls off considerably. It is, therefore, generally better as far as possible to leave a store of coal alone once it is built and to use supplies as they arrive, for then the total loss is less than it would be if the store were continually drawn on and replaced by fresh coal. This applies almost universally, though it may not if the size of a coal is important and the coal itself is of a kind that will disintegrate under the action of the weather. If the coal is a coking coal to be used as such, a loss of coking power occurring in a short time might be permitted, but the rate at which coking power is lost is so great that the loss in a longer time might be intolerable.

The more a stored coal heats the more deterioration occurs, until in the end it may take fire. Nevertheless, except for the loss of coking power, the deterioration that occurs when the temperature has followed the normal course of rising a few degrees and then falling during two or three months will scarcely be noticeable, and will be compensated for by the advantages of storing the coal.

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